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Highly active TiO_2 nanophotocatalysts for degradation of methyl orange under UV irradiation

Hiral Soni[1]*, Nirmal J.I.Kumar[1], Khushal Patel[2], Rita N.Kumar[3]

[1]P.G.Department of Environment Science and Technology (DEST), Institute of Science and Technology for Advanced Studies and Research (ISTAR), Vallabh Vidyanagar -388120 (Gujarat), (INDIA)

[2]Ashok and Rita Patel Institute of Integrated Study and Research in Biotechnology and Allied Sciences, New Vallabh Vidyanagar-3888121 (Gujarat), (INDIA)

[3]Department of Bioscience & Environment Science, N.V.Patel college of Pure and applied sciences, Vallabh Vidyanagar -388120 (Gujarat), (INDIA)

E-mail: nirmalkji@gmail.com

ABSTRACT

This study describes the application of novel chemistry methods for the removal of dye by nano-structured titanium oxide (TiO_2) photocatalysts. Such materials can be applied in the development of efficient photocatalytic systems for the treatment of water. Nanocrystalline TiO_2 was synthesized by Sol-Gel route using titanium tetraisopropoxide as a metal precursor. The catalysts were characterized by X-ray diffraction (XRD), Transmission Electron Microoscopy (TEM), Fourier-transform infrared spectroscopy (FT-IR). Synthesized TiO_2 was related to anatase phase and crystalline structure was characterized by XRD. Cuboidal and uneven shape of TiO_2 nanoparticles were observed by TEM images. FTIR reveals the functional groups present in the synthesized TiO_2 nanoparticles. Thus synthesized TiO_2 nanoparticle was used for photocatalytic degradation of methyl orange. The photodegradation of methyl orange (MO) dye, is examined both under different dye concentration(10,20,30 and 40 ppm) and amounts of TiO2 (5,10,15 and 20 mg / 10 ml). After 15W UV-365 nm irradiation for 3 h, ca. 99.9% of MO was degraded with addition of 20mg TiO2 to solutions containing 40ppm dye. The photodegradation mechanism of the quinonoidal methyl orange using nanoparticles is low cost, eco-friendly and cost effective process in the removal of toxic dyes.

KEYWORDS

TiO_2 nanoparticles;
Photocatalytic degradation;
Methyl orange;
XRD;
TEM;
FTIR.

INTRODUCTION

Paper, dyeing, plastic and textile industries use color for dyeing their products and thus use a huge amount of water which results in the production of a dye-containing wastewater with hazardous effects on the environment[1-4]. At present, 100000 different types of dyes with annual production rate of 7×10^5 are produced. Among them textile industries consume about 36000 ton/year dye, 10 to 20 percent of which remains in wastewater[5]. The presence of these dye pollutants in water streams causes numerous problems related to their carcinogenicity, toxicity to aquatic life and easily detected and undesirable esthetic aspect[6]. Dyeing effluents are very difficult to treat, due to their resistance to biodegradability, stability to light, heat and oxidizing agents[7]. MO causes eye and skin irritation and may cause respiratory and digestive tract irritations and it is also responsible for toxic effects. In addition to standard technologies for the degradation and/or removal of dyes, several new specific technologies, the so-called advanced oxidation processes (AOPs), have been developed. Heterogeneous photocatalysis, as one of the AOPs, could be effective in the oxidation /degradation of organic dyes. The initial interest in the heterogeneous photocatalysis was aroused in 1972 when Fujishima and Honda discovered the photochemical splitting of water into hydrogen and oxygen by the UV irradiated TiO_2[8]. After that, research on the heterogeneous photocatalysis started growing rapidly[9] in many area covering water and air treatment technologies.

Among the metal oxide semiconductors, TiO_2 is widely used catalyst because of its fascinating physicochemical properties, high photoactivity, photocorrosion stability, nontoxic and low cost[10,11]. It founds its application as solar cells, gas sensors, photocatalysts, capacitors, and catalyst supports[12-16]. TiO_2 self-cleaning property can be bestowed on many different types of surface, and some TiO_2 based self-cleaning products such as tiles, glass, and plastics have been commercially available. TiO_2 self-cleaning coatings are finding increasing applications in buildings, public furniture and auto industry. The self-cleaning mechanism is mainly based on TiO_2 photocatalysis, where photo-induced electron-holes catalyze reaction on the surface[17,18]. The electrons and holes form hydroxyl radicals which are assumed to be the main reactants in the degradation of many pollutants like herbicides[19], fungicide[20], aliphatics and aromatics[21], dyes[22] and bacteria[23]. TiO_2 has many polymorphs, among which anatase TiO_2 shows the highest photocatalytic activity toward photodegradation of most organic pollutants in waste water.

In this case, photosensitization of the dye may occur upon excitation by UV-light in addition to the hydroxyl radical attacking the dye molecules. The photogenerated electrons might also transfer from the excited dye to the semiconductor particle. It can also reduce the adsorbed oxygen in the suspensions to form superoxide radicals, than the reaction between the dye radical and the other active oxygen-containing species might also occur, which can accelerate the photodegradation process of the dye[24]. In the present investigation, TiO_2 nanoparticles were synthesized via Sol-Gel route using Titanium Tetraisopropoxide as a metal precursor and was characterized by X-ray diffraction (XRD), Fourier-transform infrared absorption spectrophotometry (FT-IR), Transmission Electron Microscopy (TEM), moreover, water pollutant substance from industry, one of the dyes, methyl orange was studied in aqueous medium for photocatalytic degradation under irradiation of ultraviolet light.

METHODOLOGY

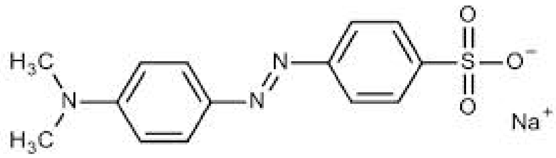
Materials

Titanium Tetraisopropoxide (97%) was provided by Sigma Aldrich Co, 3050, St.Louis, MO, USA, Glacial Acetic Acid (99%) was purchased from Hi-Media. Methyl Orange was of analytical reagent grade and used without further purification. All solutions used in the experiments were prepared by using double distilled demineralised water. The chemical structure, IUPAC name, molecular weight and Colour Index (CI) number of Methyl Orange is represented in TABLE 1.

Catalyst preparation

The Sample was prepared by novel and simple Sol-Gel route. 12 mL titanium isopropoxide was added to 23 mL acetic acid with continuous stirring. Hydrolysis of titanium tetraisopropoxide solution was carried out by adding distilled water (72 ml) slowly at the rate of 0.5 ml/min with continuous stirring. The solution was kept stirring for 6 h until achieving a clear transparent sol. Dried at 100°C, after that it was calcined at 600°C for 2 h at a ramp rate of 5°C/min.[25].

TABLE 1 : Structure and characteristics of malachite green

Dye	Methyl Orange
Structure	
λ_{max}	463nm
IUPAC name	Sodium4[(4dimethylamino)phenyldiazenyl]benzenesulfonate
M_w	327.33 g/mol
C.I.number	13025

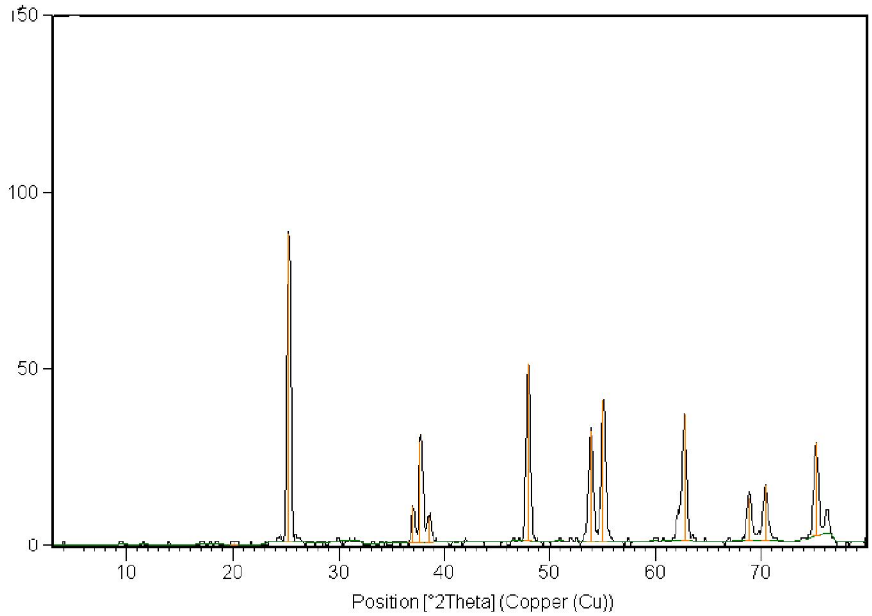


Figure 1 : XRD powder pattern of synthesized TiO_2 by sol-gel

Catalytic characterization

Powder XRD patterns were recorded with a Phillips X'pert MPD system, Holland using CuKa radiation (λ=1.5405 Aº) in a 2y range of 5–601 at a scan speed of 0.11 s^{-1} and patterns were compared with the standard anatase diffractograms[26]. Transmission Electron Microscope (TEM) studies were carried out on the sample using a model Philips Tecnai 20, Holland with an accelerating voltage of 100kV for the details of size, and morphological structure. An FT-IR spectrophotometer (SPECTRUM GX, Perkin- Elmer) was used to determine the specific functional groups in TiO2 samples. The spectrum is recorded in the range of wave-number 400–4,000 cm^{-1}.

Photocatalytic experiment

The photocatalytic activities of the materials were studied by examining the degradation reactions[27]. Methyl Orange stock containing four different concentration of dye i.e. 10ppm, 20ppm,30ppm,40ppm were prepared in borosilicate glass tubes containing various doses of synthesized catalytic TiO2 nanoparticles. Catalysts containing tubes were placed on UV- radiation lamp. Two 15 W low pressure mercury UV tubes (Spectronics) emitting near UV radiation with a peak at 365 nm were used at a light intensity of 3.48 mW/cm^2 measured near the film surface. The photocatalytic oxidation process started when UV radiation reached the TiO2 photocatalyst. Afterwards at one hour time interval sample were collected, centrifuged and analyzed with a UV-Vis spectrophotometer. A blank study was also carried out only in the presence of UV light without any catalyst. This shows that though during UV irradiation, direct photolysis of dyes could occur, mineralization of dyes only takes place in the presence of a photocatalyst[28]. In the photo degradation experiments the extent of removal of the dye, in terms of the values of percentage removal has been calculated using the following relationship:

Percentage Removal (%R) = 100*(Ci-Cf)/Cf (1)

Where, Ci= initial concentration of dye (ppm); Cf = final concentration of dye (ppm) at given time.

RESULTS AND DISCUSSION

Crystallinity and crystallite size

The photocatalytic activity of catalyst was greatly affected by its crystal structure and crystal phase. The crystal structure and crystal phase characterization of pure TiO2 is investigated. Generally, the anatase phase is reported with high photocatalytic activity than Rutile. The XRD patterns of samples are shown in Figure 1. In TiO2 sample in the present investigation, Anatase phase was detected. The average crystalline size calculated by applying the Scherrer formula on the anatase diffraction peak at 2 θ =25.28º (101), 2 θ =37.74 º (004), 2 θ =48.08 º (200), 2 θ =53.93 º (105) and 2θ=62.79 º (204). The preferred orientation corresponding to the plane (101) is observed in the sample. All the peaks in the XRD patterns can be indexed as anatase phases of TiO2 and the diffraction data were in good agreement with JCPDS files # 21-1272[29]. It should be noted that only Anatase TiO2 is detected and no Rutile phase can be found in the sample[30]. Crystallite size was also obtained by Debye-Scherrer's formula given by equation

D=Kλ/ (βcosθ)

where D is the crystal size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα; K is usually taken as 0.89; and β is the line width at half-maximum height[31]. The relatively wide width of the peaks indicates small crystallite size, which was estimated to be approximately 24 nm using Scherrer's equation from the XRD peak broadening analysis at (1 0 1)[32]. It is worth to note that the crystallite size was in the range of 20–30 nm, which is known to be optimum for high catalytic activity. This is because a very small crystallite size causes a blue shift in the light absorption spectrum and favours surface recombination of the photo-exited holes and electrons while a larger crystallite size exhibits lower surface area and thus a smaller number of catalytic active sites per unit mass of catalyst[33].

Functional group analysis of TiO_2 nanoparticles

Fourier transform infrared (FTIR) spectrum of as-synthesized anatase TiO_2 nanoparticles is shown in Figure 2. It was observed that the strong band in the range of 700–500 cm-1 is associated with the

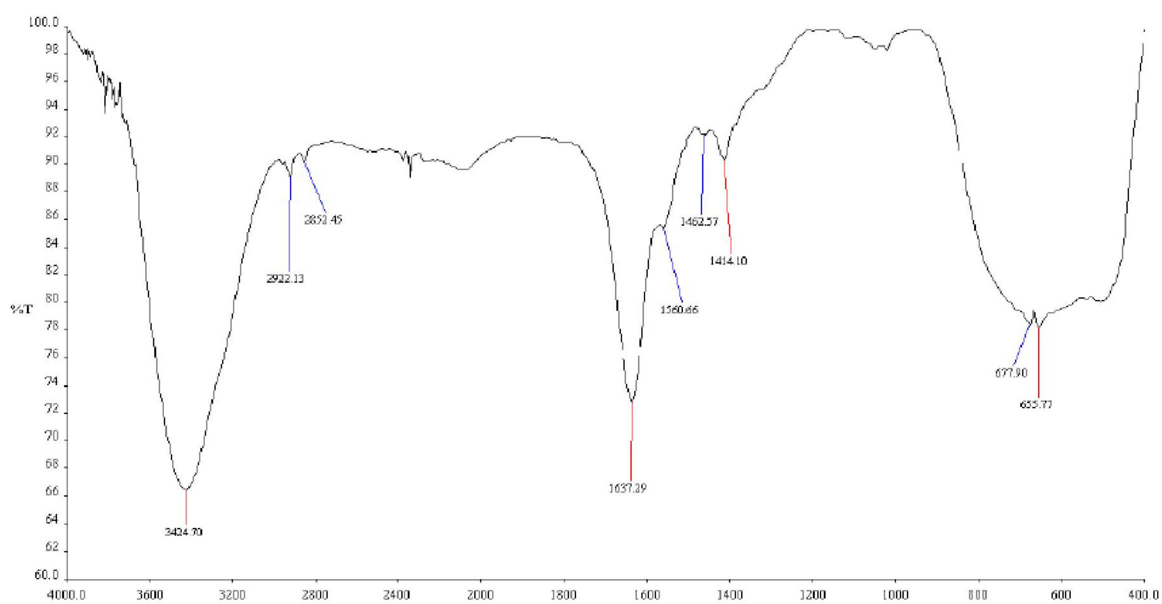


Figure 2 : FTIR spectra of synthesized TiO_2

characteristic vibration modes of TiO_2. This confirms that the TiO_2 phase has been formed. The absorption in the range from 3,500 to 2,500 cm^{-1} may be related to the presence of O–H stretching vibration (Monomer, intermolecular, intramolecular and polymeric)[34]. The absorption band at 1,637 cm^{-1} due to the presence of O–H bending vibration which is probably because of the reabsorption of water from the atmosphere has occurred[35].

Structural characteristics of TiO_2 nanoparticles

The above results indicated that the precursor titanate obtained was in nanostructure, which is further confirmed by TEM observation. The homogeneity, uniformity and the size of the resulting TiO_2 crystals were studied by TEM, as shown in Figure 2. TEM study indicated that all the crystals were completely separated from each other and uniformed with a particle analytical grade with size of 20 -30 nm. These particles do not grow together to form bigger particles, even after an extensive period of time. It is worth noting that only a small percentage of the total particles exhibit a diameter size bigger than 30 nm. The crystallites had sets of clearly resolved lattice fringes giving evidence that the TiO_2 material was highly crystalline[36].

However, there was a slight discrepancy between the particles sizes determined by XRD analysis and TEM. This could be due to the fact that the effective mass approximation is relatively less correct for small nanoparticles and statistical effects of spatial confinement also influence the optical properties of nanocrystalline semiconductors[37].

Decolorization efficiency of UV/TiO_2 photocatalysis process

Photocatalytic properties of the as-prepared samples were examined by degradation of MO dye

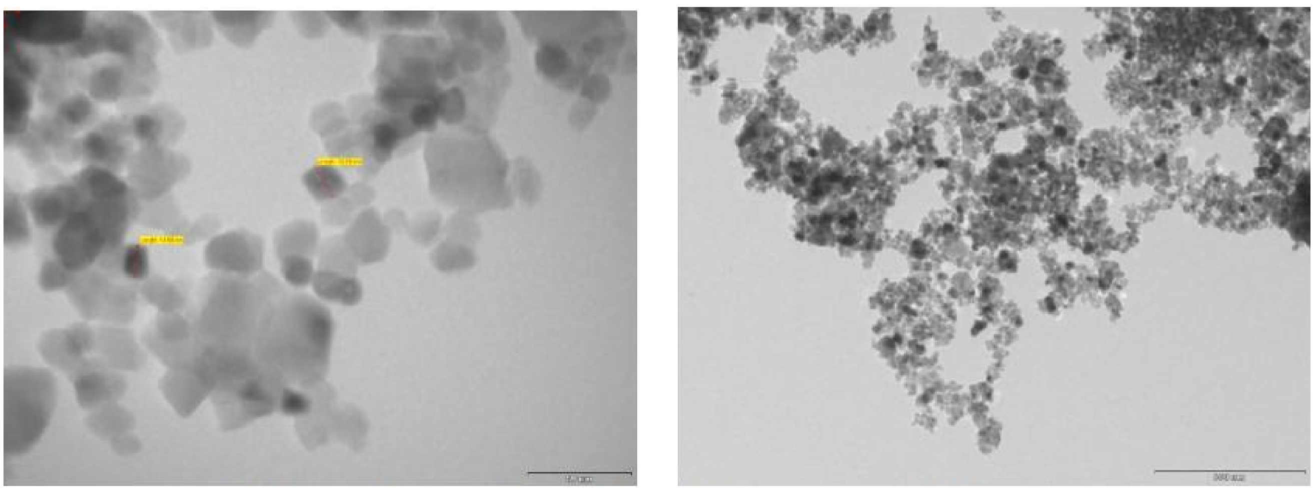


Figure 3 : TEM image of synthesized TiO_2 nanoparticles

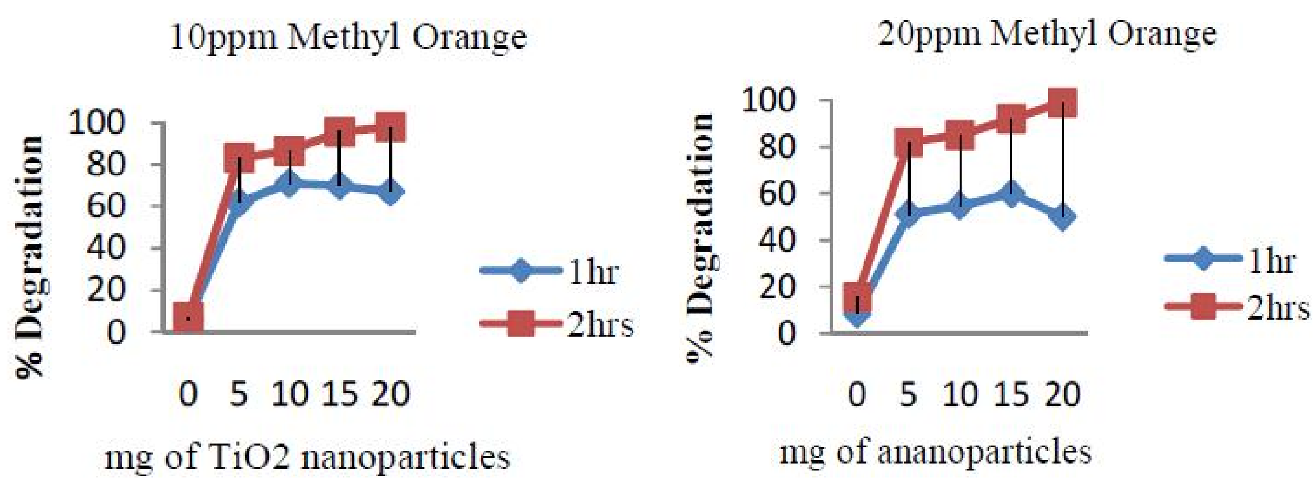


Figure 4 : Percentage decoloration vs. Dose of TiO2 nanoparticles at 10ppm, 20ppm MO

solution under UV light irradiation at room temperature. In order to identify possible losses of methyl orange in the system, control experiments without catalyst added were preformed. The course of methyl orange photocatalytic degradation used pure catalyst TiO_2 at different amount added to different dye concentration. It was found that no obvious methyl orange loss was observed in control experiment which confirmed that the methyl orange was stable in our experiment. However, four dye concentrations-10ppm, 20ppm, 30ppm, 40ppm were irradiated with different catalytic doses of 5mg, 10mg, 15mg and 20mg. At 20mg catalytic dye was found to be almost completely decolourised on irradiation for 120 minutes. Catalyst loading of 20mg showed better result than other 3 doses (Figure 4). For 30 and 40 ppm, about 60% degradation was obtained within 1 hour for 20mg concentrations of catalyst. However, 99% degradation was obtained for catalyst loading of 20mg at 3 hours (Figure 5). The degradation increases with increase in catalytic dose. There is no doubt that electron injection from the dye to the positive holes of TiO2 yields the dye cationic radical. After this stage, the cationic radical, Dye•+, can undergo hydrolysis and/or deprotonation pathway of the dye cationic radicals, which in turn are determined by the different adsorption modes of MO on the TiO2 particles surfac[38]. Total mineralization of the organic dye pollutants usually follows proposed mechanism described below[39, 40].

Photocatalysis occurs by following proposed mechanism given in step wise manner.

1. Absorption of efficient photons ($h\nu e \geq EG$=3.2 eV) by titania

(TiO2) + *hv* → e-CB+ h+VB **(1)**

2. Oxygen ionosorption (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to -1/2)

(O2)ads + e → CB→ O2•- **(2)**

3. Neutralization of OH- groups by photoholes which produces OHæ% radicals

(H2O ⇔ H+ + OH-)ads + h+VB→ H+ + OH• **(3)**

4. Neutralization of O2º- by protons

O2º- + H+ → HO2º **(4)**

5. Transient hydrogen peroxide formation and dismutation of oxygen

2HO2º- → H2O2 + O2 **(5)**

6. Decomposition of H2O2 and second reduction of oxygen

H2O2 + e- →OHº + OH- **(6)**

7. Oxidation of the organic reactant via successive attacks by OH• radicals

R + OHº → R• + H2O **(7)**

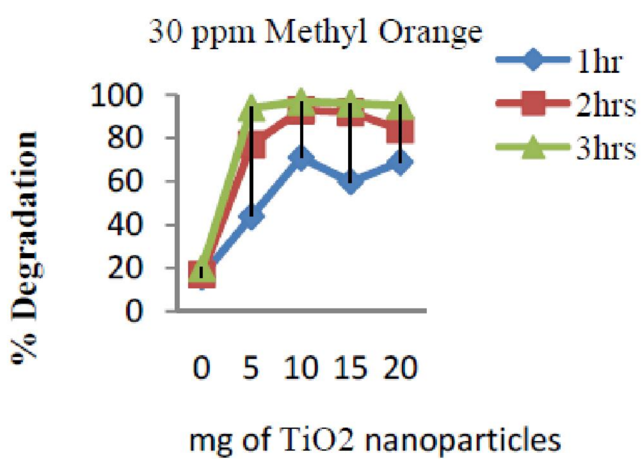
8. Direct oxidation by reaction with holes

R + h+ → R+º → degradation products **(8)**

As an example of the last process, holes can react directly with carboxylic acids generating CO2

RCOO- + h+ → R• + CO2 **(9)**

Increase in the concentration of catalyst shows an increase in dye degradation for the first few minutes. This is due to the fact that number of dye molecules adsorbed and photon absorbed increases with increase in catalyst loading. The increase in degradation was probably due to an increase in avail-



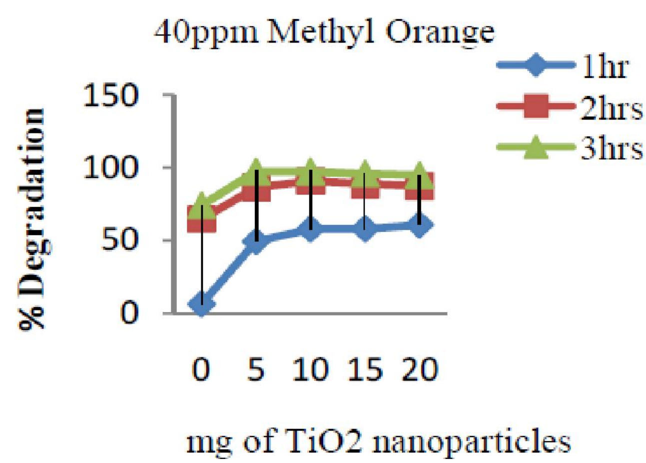


Figure 5 : Percentage decoloration vs.dose of TiO2 nanoparticles at 40ppm MO

ability of catalytic sites and adsorption sites. It could be due to decolorization of MO which undergone demethylation, methylation and hydroxylation processes.

CONCLUSION

In this research, A novel, easy and reproductive method was followed for the synthesis of TiO2and photocatalytic activity of TiO2 nanoparticles on Methyl Orange was studied. It's physical and chemical characterization was done by TEM, XRD and FT-IR. The obtained results comply with that of standard. The ultraviolet (UV) light irradiation of the dye by using nanoanatase TiO2 as a catalyst has yielded percentage decolouration of greater than 90% for a catalyst loading of 20mg and initial concentration of the dye solution of 10-40ppm.

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